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RESEARCH MEMORANDUM

DYNAMIC CORROSION OF NICKEL AT 1500° F BY SODIUM HYDROXIDE
WITH VARIOUS ADDITIVES IN A TOROID CIRCULATING APPARATUS

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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SUMMARY

Metallic sodium, sodium chloride, calcium hydride, sodium aluminate, and an alloy of aluminum were added to sodium hydroxide in individual nickel tubes and corrosion tested at a fluid velocity of 15 feet per second with a hot-section temperature of 1500° F and a hot-to-cold-section temperature difference of 20° to 30° F. A toroid circulating apparatus was used and the specimens were run for a period of 24 hours or until failure occurred. None of the additives tested resulted in a marked decrease in corrosion and mass transfer. Various methods of evaluating the severity of corrosion are discussed.

INTRODUCTION

An investigation of the dynamic corrosion behavior of molten sodium hydroxide in contact with possible container materials is being conducted at the NACA Lewis laboratory. One of the more resistant materials being investigated is nickel. Although nickel suffers no intergranular attack by sodium hydroxide at temperatures up to 1500° F, the presence of temperature differences in the system results in removal of metal from the hot zone and the formation of a crystalline metal deposit in the cold zone. The experiments herein described were carried out in an attempt to minimize this effect.

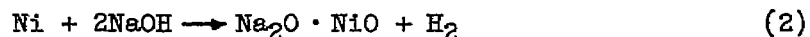
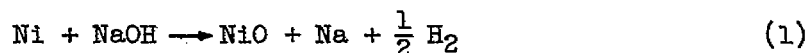
The apparatus described in reference 1 was used to circulate chemically pure sodium hydroxide (table I) at a velocity of 15 feet per second in toroids constructed from A and L nickel (table II). Specimens were run for periods up to 24 hours at nominal outer wall temperatures of 1500° F. An area approximately 1/25 of the total was maintained

at 20° to 30° F below the nominal test temperature by means of localized cooling. The effect of addition of a variety of materials to the sodium hydroxide - nickel system was investigated. They were metallic sodium, sodium chloride, calcium hydride, sodium aluminate, and an alloy of aluminum. The basis for the choice of these additives is discussed subsequently.

Various methods of evaluating the extent of corrosion are reported herein. They are based on metallographic analysis of the toroids and chemical analysis of their contents. Some of the initial results obtained (ref. 2) with this apparatus are reproduced here for comparison.

CHOICE OF ADDITIVES

Sodium. - Two alternative reactions are thermodynamically feasible for the reaction of nickel with sodium hydroxide in the hot zone. They are as follows:



The fact that a hydrogen atmosphere has been found (ref. 3) to reduce corrosion and mass transfer does not serve to distinguish between them because the addition of hydrogen would be equally effective in suppressing either reaction. On the other hand, sodium should be effective only if reaction (1) is the correct (or predominant) one. For this reason and also because sodium metal had been detected as a reaction product in other experiments, it was tested as an additive. Hydrogen rather than the usual helium was used with the sodium additions.

Hydrogen. - Hydrogen atmosphere has been demonstrated (ref. 3) to reduced mass transfer in free-convection systems. It was therefore of interest to try hydrogen under higher flow conditions. However, mechanical failure of the vent tube occurred in each of five attempts to obtain data on a toroid equipped with a constant-pressure hydrogen supply connected to the vent tube. Apparently, vibration in the vent tube made heavier by the introduction of the connections to the gas storage supply led to fatigue failure in a very short time. The occurrence of this failure despite several attempts at elaborate mounting is brought to attention here as one of the difficulties to be anticipated in the use of nickel at high temperatures.

Sodium aluminate, aluminum. - Free-convection experiments reported in references 4 and 5 indicate that sodium aluminate additions result

2638 in reduced mass transfer. However, the additions reported were in excess of the solubility of the aluminate in sodium hydroxide. Consequently, there was some doubt as to the mechanism by which the inhibition of transfer occurred, since the aluminate may have mechanically blanketed the hot zone and thus prevented reaction. That the latter might be the case is indicated by the fact that the thermal harp tests of reference 5 show that the aluminate is not beneficial. A test of aluminate addition under higher flow conditions was therefore performed to resolve the question. Aluminum is known to react with sodium hydroxide at temperatures much lower than 1500° F to form sodium aluminate (ref. 6); the first test was performed with the addition of Dural (95 percent aluminum), because it simplified the experimental procedure.

Calcium hydride. - Beneficial results were obtained in free-convection tests with additions of calcium hydride (ref. 4). Accordingly, a toroid was run with a calcium hydride concentration equal to that reported in reference 4 to have yielded the best results.

Sodium chloride. - Sodium chloride was run to verify its inertness in the system.

PROCEDURE

Fabrication of specimens. - Each specimen was made from a length of 0.63-inch outside diameter by 0.06-inch wall nickel tubing bent into a toroid with a mean diameter of 15.5 inches (fig. 1). A small bore vent tube was heliarc welded to each specimen near the closure.

The tubing bore was degreased and acid cleaned according to the procedure recommended in reference 7. Into each specimen was placed 108 grams of chemically pure sodium hydroxide pellets, which occupied approximately 40 percent of the toroid volume when molten.

A sleeve was heliarc welded over the juncture of the butted tubing ends after the toroid was loaded. A mass spectrometer leak detector was used to determine that no leaks existed in the welded areas.

Eighteen equally spaced chromel-alumel thermocouples were spot-welded to the outside wall of each toroid, sixteen of which were attached to a multiple-point temperature recorder. One thermocouple located in the middle of the hot zone was used for temperature control. The remaining thermocouple located near the entrance to the cold zone was used in the event of a control thermocouple failure. The thermocouple junctions were covered with pieces of asbestos paper to shield them from the heaters which covered the specimen surface. After approximately 0.6 inch of asbestos tape was wrapped on the hot section, the instrumentation was complete.

In order to remove the entrapped air and water vapor from the sodium hydroxide pellets, the toroids were evacuated while gradually being heated to just above the melting point of the caustic. When an indicated vacuum of approximately 5 microns was obtained at this temperature, each specimen was filled with the desired cover gas, the vent tube was crimped shut, and the end sealed with silver solder.

Installation. - Specimens were mounted on the table of the circulating apparatus by six clamps, as shown in figure 2, and the thermocouples and heaters were connected. The cooler, an annular chamber arranged to discharge compressed air through holes drilled in the inner shell, was so situated that a thermocouple was centrally located in the cooled zone.

Operation. - Electric power was supplied to the heaters until the lowest temperature on the outside surface of the toroid was at least 650° F. The mounting plate speed was gradually increased from zero to test speed (corresponding to a fluid velocity of 15 ft/sec for all tests reported herein). Power to the heaters was then increased until the insulated portion of the specimen reached 1500° F, test temperature for these specimens. An automatic controller maintained this temperature for the duration of the run. The flow of air to the cooler was then started, resulting in a temperature drop of 20° to 30° F. The magnitude of the temperature drop was limited by the electric power available to the heaters, approximately 2500 watts.

On completion of a run, the duration of which ranged from 5 to 24 hours, the toroid was opened with a tubing cutter. The contents were dissolved in water and analyzed, and any evolved gases were collected and identified. After the toroid was thoroughly washed, it was sectioned by making transverse cuts through the tubing between thermocouples. Visual inspection of all sections was followed by microscopic inspection of metallographic specimens from the hot and cold sections. A measure of the extent of mass transfer was obtained by determining the ratio of the weight of a specimen from the middle of the cooled sector to one ground to the same external dimensions from the middle of the hot sector.

RESULTS

The results of the experiments are shown in table III. Data for specimens 7 and 8 are reproduced from reference 2 for purposes of comparison. The extent of corrosion and mass transfer can be compared on three different bases: cold-to-hot weight ratio, thickness of deposit in the cold zone, and contamination concentration in the caustic. The weight ratio proved to be the most consistent of these and is plotted as a function of test duration in figure 3. The depth of the deposit in the cold zone was unreliable as a means of the extent of transfer: Examination of the cold sectors revealed that the crystal size of the

deposit (and hence the density) varied unpredictably from specimen to specimen. Chemical analysis of the water solution of the contents of the toroids showed that the caustic was contaminated with constituents of the container material. It is interesting to note that, in this particular system, the contaminant concentration can also be used as a measure of the extent of transfer (fig. 4).

Photomicrographs of specimens taken from the hot and cold sections of a typical toroid (specimen 8) are shown in figure 5. In general, the hot sections exhibited no intergranular penetration, and the cold sections showed a buildup of nickel crystals. However, in the case of the calcium hydride addition, intergranular attack to a depth of approximately 0.016 inch was observed. The sodium aluminate addition resulted in a thin green film in the hot zone and a heavier green deposit in the cold zone. The green deposit in the cold zone proved to be composed of coated nickel crystals.

The results with sodium addition give strong evidence that it is not a primary reaction product. Acceleration rather than inhibition occurred. A 4-percent addition resulted in plugging of the tube in $10\frac{1}{2}$ hours. The lack of hydrogen evolution on solution of the melt showed that the sodium had reacted with the sodium hydroxide. It is probable that the latter reaction resulted in the formation of sodium oxide which would immediately react with nickel to form nickel oxide and thus increase the transfer rate. The small quantity of hydrogen present could not be expected to counteract this.

The sodium aluminate addition yielded a result which is in agreement with the lack of inhibition reported for thermal harp tests. It is concluded that the effect of the aluminate in the free-convection tests was purely mechanical and, therefore, of no use in flow systems. The fact that Dural additions resulted in increased transfer is assumed to be due to the presence of the other components in the alloy.

Calcium hydride accelerated mass transfer under induced flow conditions and, in addition, covered intergranular attack, while sodium chloride addition was completely inert as predicted.

SUMMARY OF RESULTS

A corrosion investigation was conducted with molten sodium hydroxide flowing at a velocity of 15 feet per second, a temperature of 1500°F , and a hot-to-cold-section temperature difference of 20° and 30°F in nickel tubes. In addition to determining the effects of additions of metallic sodium, sodium chloride, calcium hydride, sodium aluminate, and an alloy of aluminum, various methods of evaluating the effects of corrosion were investigated. The investigation revealed that:

1. Sodium chloride and sodium aluminate were inert as additives.
2. Sodium, calcium hydride, and Dural caused an increase in the corrosion rate. A 4-percent addition of sodium resulted in plugging of the tube in $10\frac{1}{2}$ hours.
3. The hot-to-cold-section weight ratio proved to be the most useful measure of the extent of corrosion. The weight of dissolved constituents in the sodium hydroxide is also usable. The depth of deposit in the cold section was not useful, because the crystal size and density of the deposit varied unpredictably.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 1, 1953

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TABLE I. - ANALYSIS^a OF SODIUM HYDROXIDE PELLETS

Material	Percent by weight
Assay (NaOH)	97.6
Chlorine (Cl)	.005
Iron (Fe)	.001
Other heavy metals (as Ag)	.000
Carbonate (Na ₂ CO ₃)	.32
Phosphate (PO ₄)	.000
Silica and NH ₄ OH precipitate	.000
Total nitrogen (as NH ₃ , NO ₂)	.001
Sulfate (SO ₄)	.000

^aAs per label and verified by analysis at the time of use.

TABLE II. - NOMINAL ANALYSIS OF "A" NICKEL (99.4 Ni + Co)

Constituent	Percent by weight
Nickel	99 min
Copper	.25 max
Iron	.5 max
Manganese	.35 max
Silicon	.5 max
Carbon	.2 max
Sulfur	.02 max

TABLE III. - CONDITIONS AND RESULTS

[Weight of NaOH, 108 g; fluid velocity, 15 ft/sec.]

Specimen	7 ^a	8 ^a	29	9	11	20	32	33	28
Toroid material	A nickel	A nickel	A nickel	A nickel	A nickel	A nickel	L nickel	L nickel	A nickel
Duration of test, hr	8.5	21	23.5	5	10.5	15.7	10.6	24	24
Temperature, °F									
Hot sector	1500	1500	1500	1500	1500	1500	1500	1500	1500
^b Δt	20	20	20	20	20	30	20	20	20
Additive material	None	None	None	Na	Na	Dural	NaAlO ₂	CaH ₂	NaCl
Percent by weight	----	----	----	1	4	< 1	10	1	5
Cover gas	He	He	He	H ₂	H ₂	He	He	He	He
H ₂ evolved on solution of NaOH, liters	-----	< 0.001	< 0.001	None	< 0.001	< 0.001	-----	-----	0.001
Total contaminants in solution, g	0.183	0.303	0.252	0.375	0.674	0.366 ^c	-----	0.890 ^c	0.261
Analysis of contaminants, percent									
Ni	88.2	88.0	93.4	89.6	48.4	84.7	-----	93.7	91.7
Fe	3.8	5.9	4.8	3.1	15.9	3.3	-----	2.5	6.5
Cu	3.2	4.0	0.02	0.5	6.1	0.03	-----	0.1	0.1
Mn	2.8	1.5	1.2	4.3	25.5	4.9	-----	3.1	1.0
Cr	1.7	0.3	-----	0.2	1.1	-----	-----	-----	-----
Co	0.3	0.3	0.6	2.3	3.0	1.6	-----	0.6	0.7
Al	-----	-----	-----	-----	-----	5.5	-----	-----	-----
Maximum thickness of deposit in cold ^d sector, in.	0.015	0.012	0.008	0.010	0.250 (plugged)	0.037	0.020	0.048	0.012
Deposition ratio, in./yr	15.5	5.01	2.92	17.55	209	20.7	16.5	17.52	4.39
Weight ratio, cold-to-hot	1.06	1.10	1.09	1.07	2.05	1.25	1.05	1.26	1.09

^aReported in ref. 2.^bTemperature difference between hot and cold sectors.^cDoes not include weight of additive.^dUniform attack in hot sector, corrosion layer less than 0.001 in.

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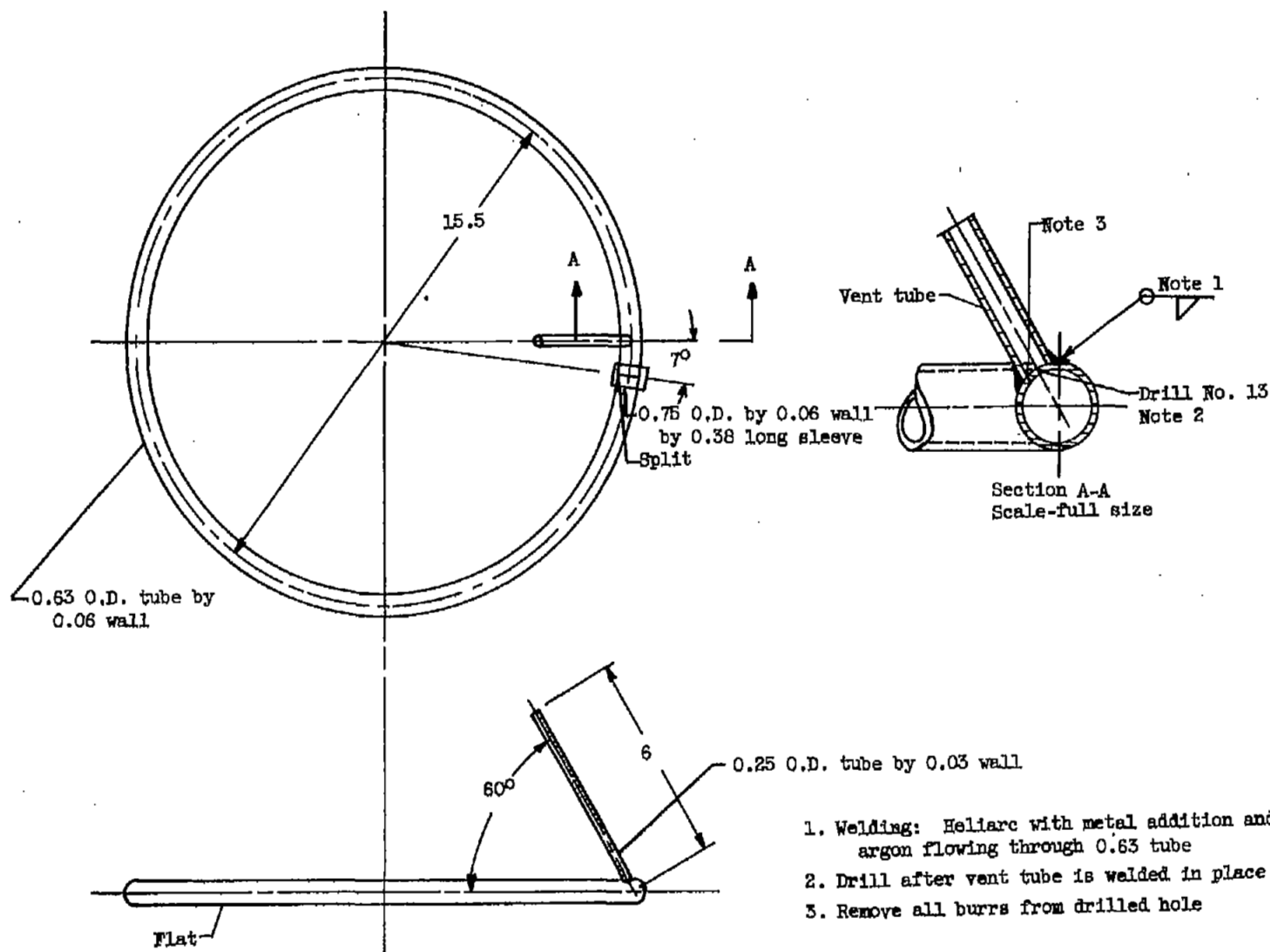


Figure 1. - Fabrication drawing of specimen.

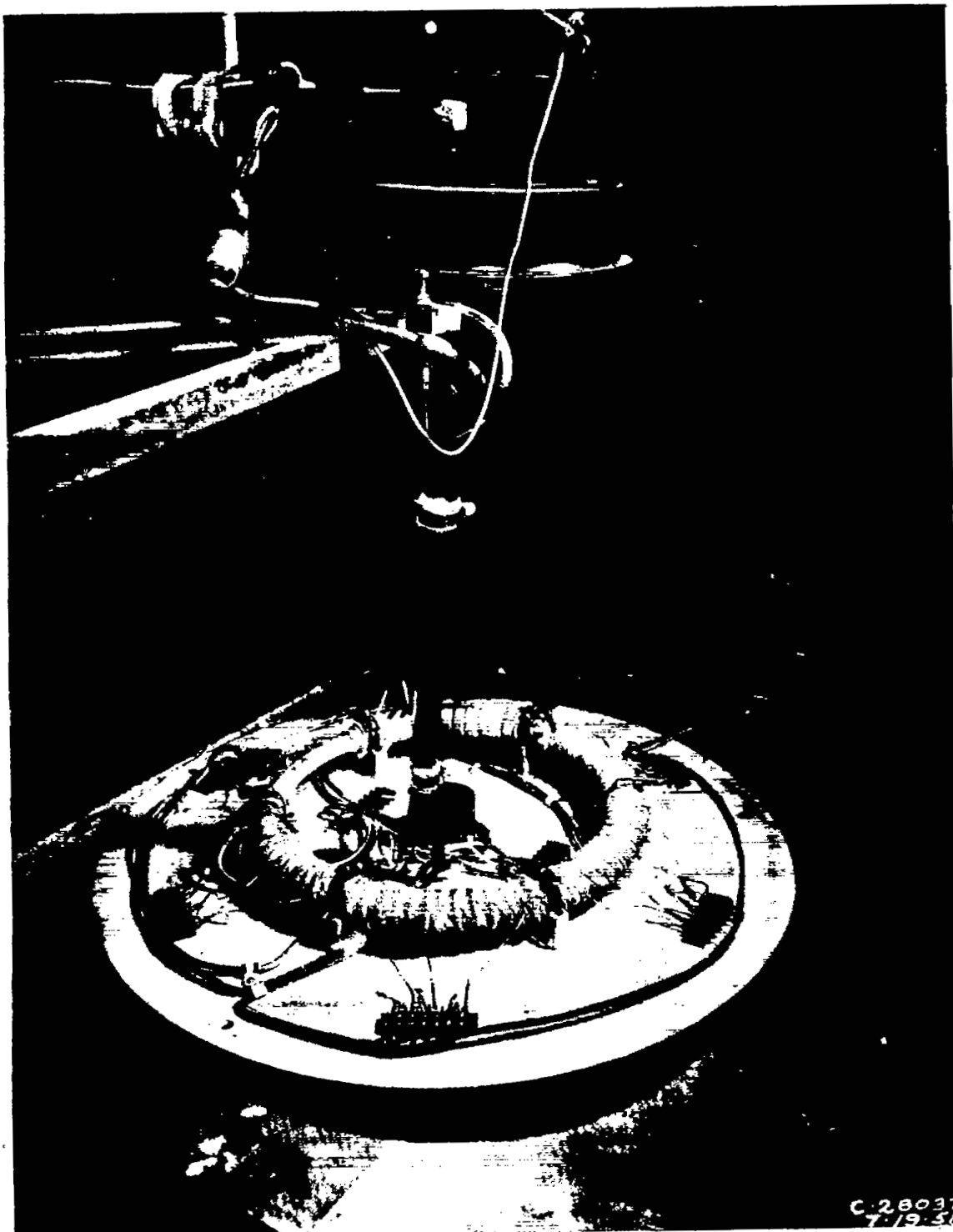


Figure 2. - Instrumented specimen installed in circulating apparatus.

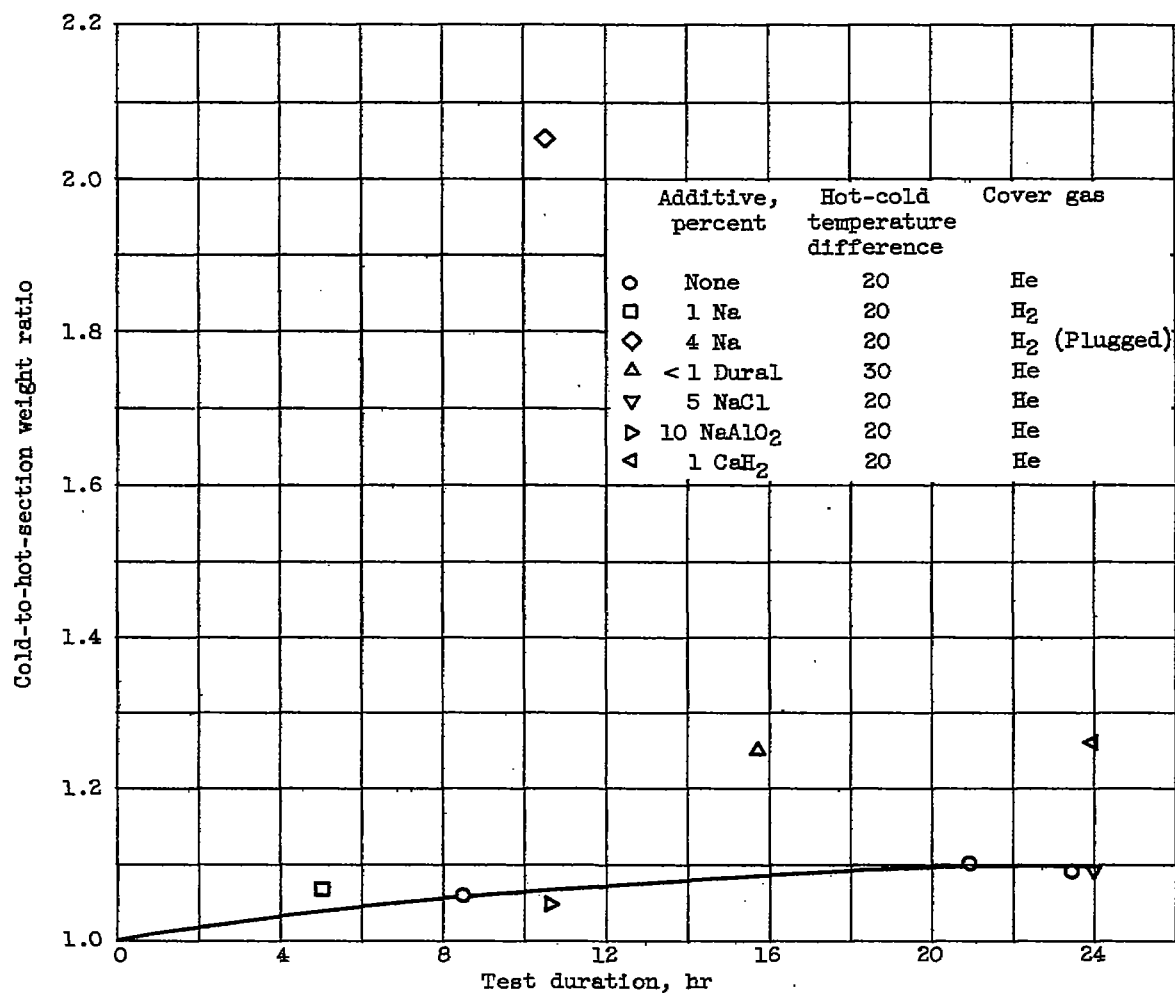


Figure 3. - Cold-to-hot-section weight ratio as a function of test duration. Sodium hydroxide flowing in type A nickel specimens at velocity of 15 feet per second and a hot section temperature of 1500° F.

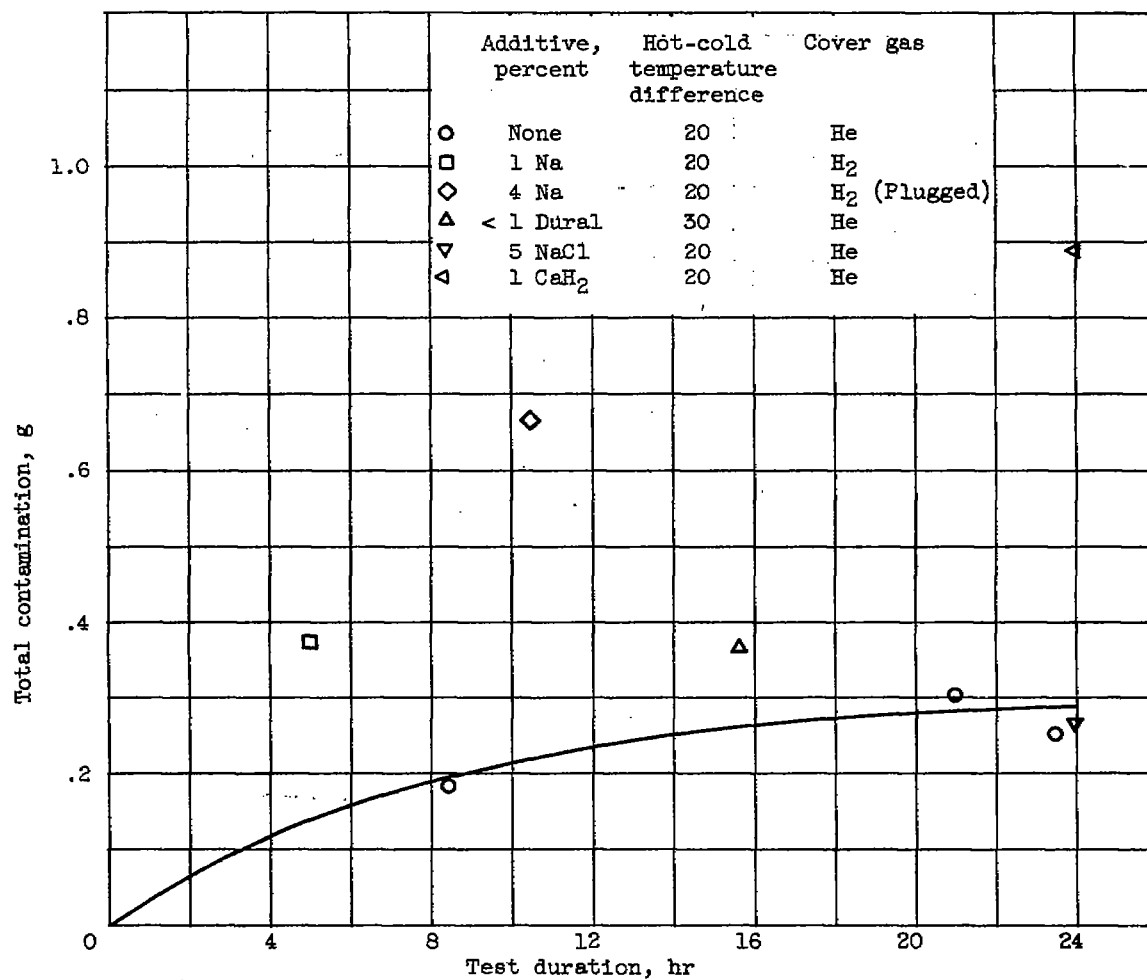
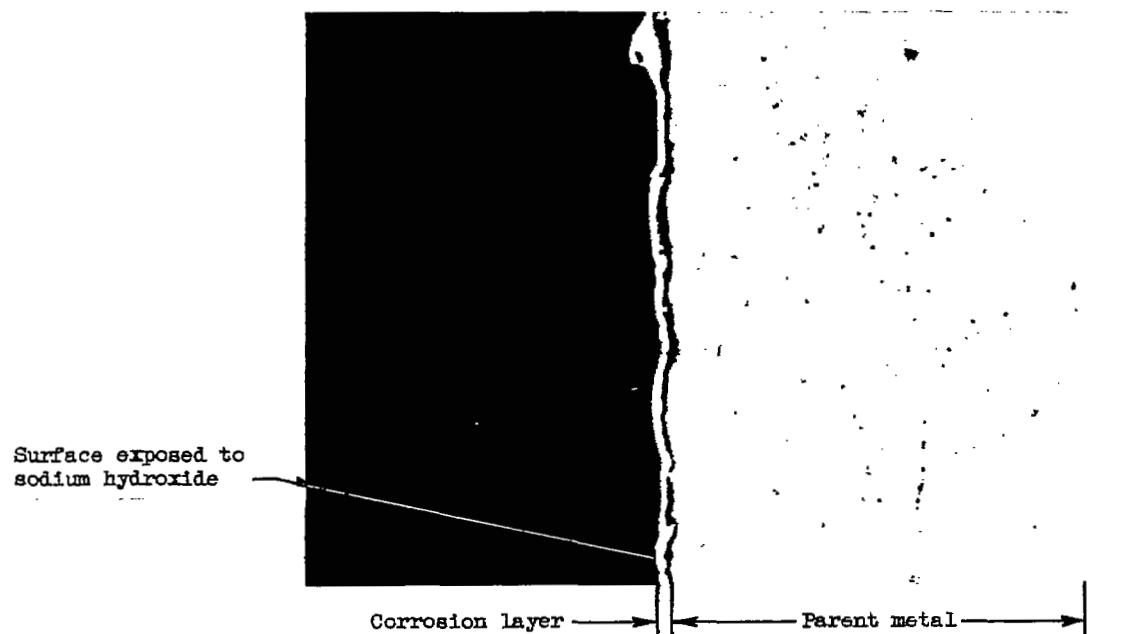
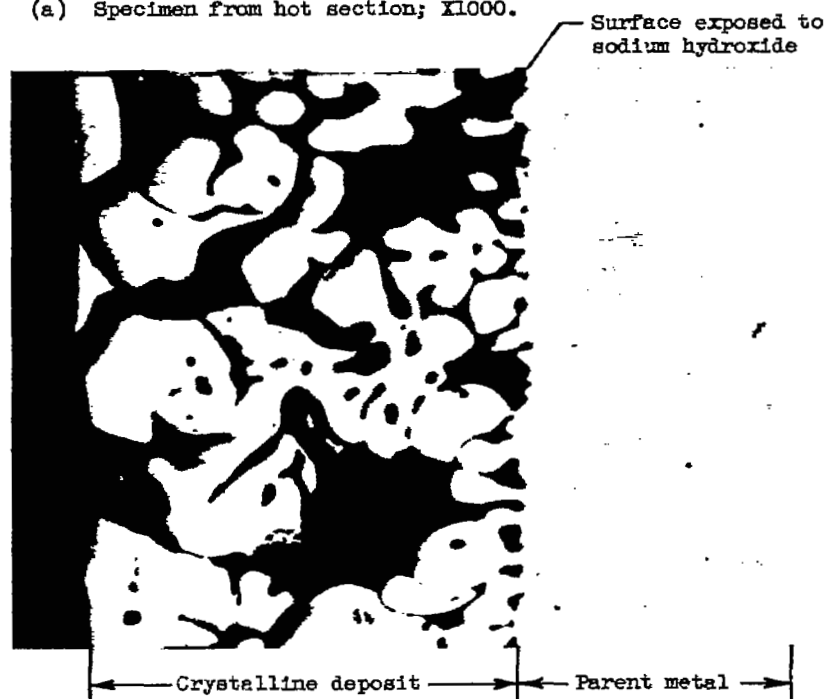


Figure 4. - Total contamination during various test durations. Sodium hydroxide flowing in type A nickel specimens at velocity of 15 feet per second and hot-section temperature of 1500° F.



(a) Specimen from hot section; X1000.



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(b) Specimen from cooled section; X250.

Figure 5. - Photomicrographs of type A nickel (specimen 8); etchant, none.

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